CHARACTERIZATION OF THE INITIAL WEATHERING OF PETROLEUM HYDROCARBONS BY FTIR SPECTROSCOPY AND SUPERCritical FLUID CHROMATOGRAPHy

Lamya Mansur and Alan Williams
Department of Fuel and Energy
Leeds University
Leeds LS2 9JT, United Kingdom

Keith D. Bartle and Mark W. Raynor
Department of Physical Chemistry
Leeds University
Leeds LS2 9JT, United Kingdom

ABSTRACT: Chemical changes resulting from the weathering processes of oils have been investigated on a bench scale weathering apparatus. A multicomponent oil simulating crude oil was developed for this purpose. Hydrocarbon concentrations resulting from evaporation and dissolution were measured using Fourier transform infrared (FTIR) spectroscopy and interpreted by a computer program (CIRCOM), which uses the method of principal components regression for multicomponent quantitative analysis. This method could be fast and accurate for quantitative assessments of changes in chemical and physical properties of an oil. However, this study outlines only the chemical measurements of saturated and aromatic hydrocarbon composition.

Experiments were also undertaken to study weathering processes on oil droplets. In this technique single droplets of crude oil were suspended in water, the trends of dissolution were studied, and the behavior of the remaining heavy fraction assessed by FTIR spectroscopy and capillary column supercritical fluid chromatography (SFC). SFC was used to identify compounds, especially high molecular weight alkanes, and their changes in concentration with time in suspension in water. The results show that the main changes in the composition of oil droplets in stagnant waters are loss of low molecular weight material and differential loss of high boiling n-alkanes compared to their isoprenoid counterparts. FTIR spectroscopy and SFC proved powerful techniques for detecting minimal weathering processes, including oxidation, dissolution, and microbial degradation.

Experimental methods

Synthetic oil weathering experiment. A four-component simulated oil was gravimetrically prepared of the following hydrocarbons: n-nonane, cyclohexane, cumene, and squalane. The mixture of about 3 g was placed in a tank of distilled water about 20°C and agitated with a magnetic stirrer for two hours.

Concentrations of the hydrocarbons were measured on a Perkin-Elmer 2750 FTIR spectrometer using CIRCOM software. For this purpose, a calibration set of 20 standards was prepared to cover the range of concentrations over which the oil components were expected to vary.

Oil droplet analysis. Different techniques were implemented to study the weathering of the oil. Droplets about 1 mm in diameter of Kuwait crude oil were suspended by a wire loop and immersed in distilled water without agitation. After timed periods, samples of the water and of the remaining oil on the wire loop were analysed as follows:

FTIR measurements. The suspended oil droplets were extracted in n-pentane and dried with anhydrous magnesium sulphate. Full spectra were obtained by loading the samples on KBr cells, while absorption at specific wave numbers was studied by adding the KBr powder to the samples and pressing them at 10 tons pressure to form pellets.

The water phase was extracted in a separator funnel with carbon tetrachloride and dried with anhydrous magnesium sulphate. The samples were analyzed in 10 mm glass cells for better detection of small amounts of hydrocarbons.

Capillary SFC measurements. A Lee Scientific series 600 capillary SFC instrument (Dionex) was used for this study. SFC grade carbon dioxide (Air Products) was pressurized by the pump in liquid form and delivered to a Valco CHW microvalve injector with a 200 nL sample loop. The injector was held at room temperature during each chromatographic run and was rapidly switched for a time-split injection of the samples in solution in CH2Cl2 into the capillary column. A
Figure 1. Variation of percentage mass of hydrocarbons in synthetic oil mixture with time as measured by multicomponent analysis.

Results and discussion

Multicomponent analysis. Computer software (CIRCOM) was used to assess the changes in the concentrations of the synthetic oil components from their corresponding IR spectra.

Data processing algorithms used in FTIR rely on the intensities of spectral bands being linearly proportional to the concentration of each component in the samples. This is the Bouguer-Beer-Lambert law, which gives the total absorbance at any wave number $\nu$ for a mixture of $N$ components as

$$A(\nu) = \sum_{i=1}^{N} a_i(\nu)bc,$$

where $a_i(\nu)$ is the absorptivity at $\nu$, $b$ is the path length, and $c$ is the concentration of the samples. This assumption allows the use of factor analysis that condenses the information of the mid IR spectra into a manageable form. Factor analysis uses a matrix algebraic technique, which in CIRCOM is a product-moment matrix:

$$Z = D^T D$$

where $D$ is a matrix of $n_r$ rows by $n_c$ columns of the spectra of a set of well-characterized samples. This gives the minimum number of factors required to reproduce the spectra within experimental error,
Figure 3. FTIR spectra (C-H stretch) of (A) oil droplets suspended in water for different periods and (B) water phase

together with the coefficients of the factors for each spectrum. Statistical correlations (multiple linear regression) are then used to estimate the properties of the unknown samples.

**Weathering prediction.** Changes in the composition of the synthetic oil during stirring in water can be attributed to both evaporation and dissolution. Figure 1 shows the changes in hydrocarbon concentrations.

Although cyclohexane and squalane concentrations are found in agreement with other studies, concentrations of cumene and nonane are found in less than expected values. The rate of loss of low boiling hydrocarbons was greatest within the first 90 minutes through evaporation and dissolution.

Consistent results were obtained with different calibration sets and different component concentrations, showing that the high molecular mass of squalane (422.83 daltons) might have affected the behavior of the synthetic mixture. However, the good repeatability of the method and its accuracy and speed permit the detection of the weathering rates of a much larger number of components, capabilities that could be used in the algorithms of oil spill weathering models.

**Spectral subtraction.** The suspended oil droplets were used mainly to study the behavior of oil particles dispersed in the water column. This behavior is of special importance in oil spill weathering studies, because most of the hydrocarbons present in the water column under a slick are in dispersed form, and any dissolved hydrocarbons present

Figure 4. Changes of ratio of CH₃/CH₂ absorptions for oil droplets and water with time
probably were obtained by dissolution from the dispersed oil particles.

The IR spectra of the oil droplets during weathering were subtracted to detect any molecular changes (Figure 2), since constant features are removed by the subtraction operation. Small spectral differences are easy to determine by this method and new bands appear as positive absorbances. The absorption in the region 1776–1780 cm⁻¹ indicates the presence of oxidative weathering in the droplets. The downward shift in the baseline at certain wavenumbers in the 1300–900 cm⁻¹ region are also indicators of weathering of the oil droplets, with the peaks at 1165, 1145, 1070, and 1032 increasing the most compared to those at other wavenumbers.¹

Interpretation of specific spectral regions. More detailed information of the chemical changes in the oil is obtained by following the absorptions arising from C-H stretching in the alkanes (3000–2840 cm⁻¹), for both the oil droplets and the water (Figure 3). The band at 2960 cm⁻¹ is indicative of methyl groups, that at 2930 cm⁻¹ of methylene. Analysis of the oil droplets showed little variation in the CH₃/CH₂ ratio (Figure 4), which indicates a relatively small change with time in the composition of the oil droplets suspended in water. The water, however, showed an increase in the CH₃/CH₂ ratio and a subsequent decrease, which indicates dissolution of branched structures. The aromatic C-H stretching band, which occurs between 3100 and 3000 cm⁻¹, did not appear on the spectra due to the weak C-H stretch in aromatic compounds and the small extent of dissolution. Dissolution of aromatics is expected to have taken place, however, since low boiling aromatics are depleted relative to saturated compounds.²

SFC measurements. An octylsiloxane-coated column was chosen for SFC, since, in this stationary phase the retention behavior of alkanes and aromatics with similar boiling points is almost identical.³

Analysis of the original Kuwait crude by SFC (Figure 5A) and comparison with the retention behavior of standard compounds revealed the presence of n-alkanes up to ~C₅₀ superimposed on an unresolved envelope of branched/cyclic and aromatic hydrocarbons extending to a retention corresponding to a boiling temperature beyond 400°C. Peaks from the isoprenoidal hydrocarbons pristane and phytane were also clear. Typical spectra obtained after weathering (Figures 5B and 5C) show that the initial loss of low molecular weight aromatics, and n-alkanes up to C₁₅, was rapid and almost complete after one day's immersion. Thereafter, there was a slower loss of C₁₅–C₂₂ alkanes and little apparent change in the underlying envelope or in the concentration of very high molecular weight compounds (Figure 6A); this loss is much less than in chromatograms of oils weathered on sea surfaces.⁷ Those observations are consistent with our previous IR spectra.

In addition, the results showed that the loss of higher boiling n-alkanes compared to branched alkanes is also slower (Figure 6B). However, the decrease in the ratio of n-alkanes to isoprenoids after three days' immersion shows that n-alkanes are depleted through microbial action, since n-alkanes are more readily biodegraded than isoprenoids. This suggests that microbial degradation is the dominant mechanism for the loss of n-alkanes from suspended oil droplets, and not dissolution.

Conclusion

This study has shown that IR spectroscopy, which has been used for fingerprinting of oils and their weathered samples,⁷ could also account for weathering processes both quantitatively and qualitatively.

Factor analysis of the IR spectra of a synthetic oil determined the evaporation and dissolution rates of the oil components. With a larger number of components, this can assist the development of pattern recognition procedures to improve weathering predictions. IR spec-
troscopy was also capable of detecting limited rates of dissolution and oxidation processes.

SFC was successful in identifying petroleum hydrocarbons and their weathering trends. The rapid loss of low molecular weight compounds was evident. Later changes were slower than in natural weathering in seawater. SFC has been shown to be a powerful technique for the characterization of the higher boiling fractions and distinguishing between isomers, which is of special importance in oil spill weathering studies and which is still difficult to accomplish by hyphenated GC techniques. The rapid loss of low molecular weight compounds only was evident. Later changes were slower than in natural weathering in seawater.

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References
